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8. ELASTOMER SEAL COMPATIBILITY

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8.1 Introduction

Excessive swelling or deterioration of the elastomer seal (o-ring and its lubricant) in the fire suppressant storage container could lead to leakage of the agent leaving the system unready to respond in case of fire. Short term exposure experiments have been conducted and data have been generated on the proclivity of the eleven fluid agents to alter the properties of various elastomers and greases. The compatibilities of the fire suppressant agents with commonly used elastomers and greases have been characterized using two types of measurements.

The first type was based on solution thermodynamics and characterizes swelling due to sorption of the agent into the elastomer or grease. The degree of swelling was determined by measuring the solvent (agent) weight fraction w_1 in the polymer (elastomer or grease)/solvent (agent) system at various temperatures and vapor pressures. Using these weight fractions and the Flory-Huggins theory (Flory, 1942; Huggins, 1943), a single polymer-solvent interaction parameter χ was calculated for each polymer/agent system at various temperatures. The χ values were used to characterize the compatibility of the solvents (agents) with the polymers (elastomers and greases). Small χ values correspond to good solubility or, for present purposes, bad compatibility. Above $\chi = 0.5$, the solubility of polymers gradually decreases with increasing χ. A rating system was defined based on the values of χ parameters obtained from swelling measurements at 35 °C. Good compatibility ($\chi > 1.2$, $w_1 < 0.22$) implies that an elastomer or lubricant is acceptable for use in the fire suppressant system. Bad compatibility ($\chi < 0.9$, $w_1 > 0.38$) corresponds to excessive swelling. For values of $0.9 < \chi < 1.2$, the agent was considered to have fair compatibility with the elastomer or grease and represents a marginally acceptable system.

The second type, durability measurements, produced data on residual mechanical (rheological) properties of the elastomers (greases) after exposure to the fluids at elevated temperature and pressure (150 °C, 5.86 MPa). Compatibility ratings were based on the results of compression set and tensile test measurements of the elastomers and viscosity measurements of the greases. These tests provide direct information on the physical and chemical damage to the samples at extreme conditions. While the following procedures were used to define the fire suppressant agent/elastomer or lubricant compatibilities, it is important to note that the long term exposure response of these materials cannot be extracted from the tests as performed. A major conclusion from the results of the durability testing is that the 150 °C condition is too severe, *i.e.*, property changes for the most-part were extreme. Further testing at lower temperatures will be required to provide better estimates of elastomer and lubricant durabilities in the final down-selected candidate fluids.

In compression set measurements, good compatibility was defined as a condition when the compression set (percent of original deflection retained after release from compression) was less than 90% after a 2 week exposure. Elastomers have bad compatibility if the compression set exceeded 90% after 4 weeks. If the compression set was less that 90% after 2 weeks but exceeded 90% after a 4 week exposure, the agent was considered to have fair compatibility with the elastomer and represents a marginally acceptable system. If a specimen was split or broken, the agent was considered to have bad compatibility with the elastomer.

In the tensile test measurements, good compatibility was defined as a condition when the decrease in ultimate elongation (percent increase of inner circumference at rupture) was less than 65% after a 4 week exposure. Elastomers have bad compatibility if the decrease in ultimate elongation exceeded 65% after a 2 week exposure. If the decrease in ultimate elongation was less than 65% after 2 weeks but exceeded 65% after 4 weeks, the agent was considered to have fair compatibility with the elastomer and represents a marginally acceptable system.

The viscosity of the greases, when measurable, did not show systematic variation with exposure time, indicating that no significant chemical degradation occurred. It was found, however, that mobile substances or fractions were extracted by some of the candidate fire suppressant fluids which resulted in the greases becoming powder-like, *i.e.*, their viscosities were not measurable. Therefore, the ratings for the lubricant compatibility were based on the following criteria: Good compatibility was defined as a condition when the grease did not become powder-like after a 6 week exposure. Lubricants have bad compatibility if the grease became powder-like after a 4 week exposure. If the grease's viscosity was measurable after 4 weeks, but became powder-like after 6 weeks, the lubricant was considered to have fair compatibility with the agent.

The following describes the section organization: Section 8.2 describes the characterization of the agents in terms of thermodynamic swelling measurements. After briefly describing the theoretical basis of the thermodynamic investigations (Section 8.2.1), the vapor sorption experiments are described (Section (8.2.2) and the results of swelling measurements are presented (Section 8.2.3). Section 8.3 describes the characterization of the agents in terms of the durability measurements. After describing the high temperature exposure method (Section 8.3.1) and each durability measurement technique, the results of mechanical property measurements (compression set, tensile test, and viscosity) performed on the elastomers and greases are described (Sections 8.3.2 and 8.3.3). In Section 8.4, the results of the durability measurements in combination with the thermodynamic (swelling) investigations are used to characterize the compatibility of fire suppressants with elastomer seals.

8.2 Thermodynamic Compatibility

8.2.1 Theoretical Considerations. Swelling is a powerful method for characterizing the affinity of a polymer (elastomer or grease) to a solvent (fire suppressant agent). The driving force for swelling is the change in the free energy of mixing. The Flory-Huggins lattice theory of polymer solutions (Flory, 1942; Huggins, 1943) describes the free energy of mixing under subcritical conditions and characterizes the affinity of the polymer to the solvent by a single polymer-solvent interaction parameter χ. Existing network theories allow the evaluation of the relevant thermodynamic parameters from equilibrium swelling measurements when the polymer is crosslinked (James and Guth, 1943; Flory and Rehner, 1943; Flory and Erman, 1982). Proposed improvements of the theories lead to more complicated expressions containing more adjustable parameters. The corresponding states theory of polymers (Flory *et al.*, 1964a and 1964b.; Flory, 1965) provides a more general framework to analyze the thermodynamic properties of polymer systems both under subcritical and supercritical conditions.

In swelling measurements, the solvent activity is varied to swell the polymer by different amounts. In vapor sorption experiments, first conducted by Gee *et al.* (1965), the solvent uptake of the polymer is controlled by varying the partial pressure (activity) of the swelling agent in the equilibrium phase. Similar experiments have been performed by Brotzman and Eichinger (1982 and 1983) and McKenna and Crissmann (1993). The same thermodynamic information can also be

obtained using other methods to vary the solvent activity around a swollen network (Boyer, 1945; Pennings and Prins, 1961; Horkay and Zrinyi, 1982; McKenna *et al.*, 1989; Horkay *et al.*, 1989; McKenna *et al.*, 1990). However, vapor sorption experiments were used to measure the degree of swelling because of their straightforward interpretation and many polymer/solvent systems can be analyzed simultaneously.

8.2.1.1 Flory-Huggins Theory. The thermodynamics of mixing is governed by the change in free energy

$$\Delta G_m = \Delta H_m - T\Delta S_m \,, \tag{1}$$

where ΔG_m is the change in Gibbs free energy, T is the absolute temperature, ΔH_m is the heat of mixing, and ΔS_m is the entropy of mixing. A negative value of ΔG_m indicates that the mixing process occurs spontaneously. The term $T\Delta S_m$ is always positive because the entropy increases upon mixing.

The thermodynamic properties of polymer solutions both in the semi-dilute and concentrated regimes can be described in a straightforward way using the Flory-Huggins lattice theory (Flory, 1953). This theory calculates the entropy of mixing from the possible arrangements of component molecules (*i.e.*, solvent molecules and monomeric units of the polymer) with respect to each other, *i.e.*, ΔS_m is given by

$$\Delta S_m = k\,(N_1 \ln v_1 + N_2 \ln v_2) \,, \tag{2}$$

where N_1 and N_2 are the number of molecules of the solvent and polymer, respectively, v_1 and v_2 are the corresponding volume fractions and k is the Boltzmann factor. The Flory-Huggins theory calculates the heat of mixing by introducing the dimensionless interaction parameter

$$\chi = \frac{\Delta H_m}{(kTN_1 v_2)} \tag{3}$$

which when combined with Equation 2 leads to the total free energy of mixing

$$\Delta G_m = kT\,(N_1 \ln v_1 + N_2 \ln v_2 + \chi N_1 v_2) \,. \tag{4}$$

The value of χ depends on the thermodynamic quality of the solvent: in good solvent conditions $\chi < 0.5$ and in "theta" conditions $\chi = 0.5$. For poor solvents $\chi > 0.5$.

In general, χ depends on the polymer volume fraction (Flory, 1970), *i.e.*,

$$\chi = \chi_0 + \chi_1 v_2 + \cdots \,. \tag{5}$$

The chemical potential of the solvent μ_1 can be obtained by differentiating the Gibbs free energy of mixing with respect to the number of solvent moles and

$$\mu_1 - \mu_1^o = \Delta\mu_1 = RT\,[\ln(1 - v_2) + (1 - 1/P)v_2 + \chi v_2^2] \,, \tag{6}$$

where μ_1^o is the chemical potential of the pure solvent and P is the degree of polymerization. $\Delta\mu_1$ is related to measurable macroscopic quantities, such as the vapor pressure of the solvent p and the osmotic pressure of the solution Π. From general thermodynamic considerations,

$$\Delta\mu_1 = RT \ln(p/p^o) = -\Pi V_1 , \tag{7}$$

where p^o is the saturation pressure of the solvent at temperature T, V_1 is the partial molar volume of the solvent and R is the gas constant.

Combining Equations 6 and 7 yields

$$\ln(p/p^o) = \ln(1 - v_2) + (1-1/P)v_2 + \chi v_2^2 , \tag{8}$$

which can be fit to experimental data using adjustable parameters χ_0, χ_1, ... from Equation 5. Thus, chemical potentials obtained from vapor pressure or osmotic pressure measurements yield empirical values of χ. These values allow the estimation of the solubility of polymers. Small χ values ($\chi <$ 0.5) correspond to good solubility. In good solvents, crosslinked polymers exhibit a large amount of swelling which can lead to seal failure in elastomeric o-ring based joints. High χ values ($\chi > 0.5$) are characteristic of polymer/solvent systems with limited miscibility. Crosslinked polymers swell only a small amount in thermodynamically poor solvents.

The simple Flory-Huggins theory discussed above is based on a series of arbitrary assumptions (*e.g.*, lattice sites are the same size for polymer segments and solvent molecules, uniform distribution of the polymer segments in the lattice). The χ parameter is, by definition (see Equation 3), governed by the interaction energy. In reality, χ is a measure of Gibbs free energy, *i.e.*, it also contains an entropy contribution. Because of several assumptions involved in the Flory-Huggins theory, χ can only be considered an empirical fitting parameter, without precisely defined physical significance, which accurately describes the thermodynamics of the system in question.

Although the Flory-Huggins theory is formulated in terms of volume fractions (v_1 and v_2), the theory can also be expressed in terms of weight fractions (w_1 and w_2). This substitution is arbitrary, but the functional form of Equation 8 remains the same

$$\ln(p/p^o) = \ln(1 - w_2) + w_2 + \chi_0 w_2^2 + \chi_1 w_2^3, \tag{9}$$

where $\chi = \chi_0 + \chi_1 w_2$ has been substituted and the term (1 - 1 / P) has become unity since P is large for polymeric materials and infinite in crosslinked networks. Strictly speaking the use of the volume fraction in the Flory-Huggins theory is also a simplification because the surface area fraction is the relevant quantity in deriving the enthalpy of mixing on a lattice. In this case the χ values differ from those calculated from the equilibrium volume fractions (v_1 and v_2). Throughout the present report weight fractions are used instead of volume fractions because they are directly measured quantities.

8.2.1.2 Flory's Equation-of-State Theory. The principle of the corresponding state theories rests on the assumption that the intermolecular potentials for the polymer and solvent have equivalent forms when expressed as functions of the distance between molecular (or segment) centers. If the thermodynamic properties are known for one reference fluid, those for any corresponding fluids are determined by two scale factors: one for the separation distance of molecular centers and the other for the magnitude of intermolecular potential. These factors are embodied in a characteristic temperature T^* and a characteristic pressure p^*. In the case of polymers the third important parameter is the number of intermolecular degrees of freedom.

Flory formulated the partition function of liquids by combining a rudimentary factor for hard spheres with an intermolecular energy of the van der Waals form (Flory *et al.*, 1964a; Flory *et al.*, 1964b; Flory 1965). The reduced equation of state of a pure liquid is

$$\frac{\pi \upsilon}{\tau} = \frac{\upsilon^{1/3}}{\upsilon^{1/3}-1} - \frac{1}{\upsilon \tau} , \tag{10}$$

where $\upsilon = v / v^*$, $\tau = T / T^*$, $\pi = p / p^*$ are the reduced variables and v^* is the characteristic (hard core) volume. A pure component is completely characterized by the three parameters v^*, T^*, and p^*. The values of these parameters can be evaluated from *pvT* (pressure-volume-temperature) data by nonlinear regression fit to the theoretical equation of state (Equation 10). These parameters are tabulated in the literature for many small molecules as well as for several polymers (Shih and Flory, 1972).

The application of the equation-of-state theory for a two component mixture requires the knowledge of the parameters of the pure components as well as their interactions in the mixture defined by an interaction enthalpy parameter X_{12} and interaction entropy parameter Q_{12}. The chemical potential of mixing is given by

$$\begin{aligned} \frac{\Delta \mu_1}{RT} &= \ln(1 - \varphi) + (1 - 1/P)\varphi \\ &+ \frac{p_1^* v_1^*}{RT}\left[3T_1 \ln\left(\frac{\upsilon_1^{1/3} - 1}{\upsilon^{1/3} - 1}\right) + \frac{1}{\upsilon_1} - \frac{1}{\upsilon} + p_1(\upsilon - \upsilon_1)\right] \\ &+ \frac{v_1^* X_{12} \theta_2^2}{RT\upsilon} - \frac{v_1^* Q_{12} \theta_2^2}{R} , \end{aligned} \tag{11}$$

where φ is the segment fraction and θ_2 is the site fraction of the polymer.

For the mixture the reduction parameters can be calculated from

$$p^* = p_1^*(1 - \varphi) + p_2^* \varphi - (1 - \varphi)\theta_2 X_{12} \tag{12}$$

and

$$T^* = p^* / ((1 - \varphi) p_1^* / T_1^* + \varphi p_2^* / T_2^*) . \tag{13}$$

Knowing p^* and T^*, υ can be obtained from Equation 10. The only remaining unknown parameters are X_{12} and Q_{12}. Since the interaction terms usually have very little effect, X_{12} and Q_{12} are usually treated as free variables (adjustable parameters).

Equation 11 allows the calculation of the chemical potential both below and above the critical temperature of the solvent and therefore can be used to describe the solubility of a supercritical gas in a polymer. (The simple Flory-Huggins lattice theory discussed in the previous section cannot be used above the critical temperature of the fluid because the saturated pressure of the vapor p^o is not defined under supercritical conditions.)

In Section 8.2.3 some examples are shown which use Flory's equation-of-state theory to describe the experimental results both below and above T_c. This analysis has not been performed for all of the

polymer/solvent systems because the solvent uptake was relatively small above T_c at the pressures tested.

8.2.2 Swelling Measurements

8.2.2.1 Experimental Setup. The degrees of swelling of three greases and six sets of crosslinked and uncrosslinked elastomers were determined by measuring the displacement of each quartz spring using a cathetometer as in the experimental arrangement illustrated in Figure 1. The elastomer's or grease's mass uptake of the agent (solvent) was calculated from the relative displacement of the springs. The cathetometer had a vernier scale permitting readings to 0.01 mm but measurements were recorded to the nearest 0.05 mm because of difficulties in viewing the spring and pan assemblies.

Six pressure vessels were designed and built for this purpose. The pressure vessels were made of type 304 stainless steel and designed for a maximum working pressure of 5.86 MPa with two view ports 180° apart for viewing and backlighting purposes. The view ports were made with 10.2 cm diameter and 25.4 mm thick circular plates of tempered Corning Glass Pyrex (trademark for borosilicate) glass. The cylindrical vessel had 2.25 liters of inner volume (17.8 cm height by 12.7 cm diameter) and was large enough to admit a 7.6 cm square by 15.2 cm high stainless steel spring stand with sixteen fused quartz spring and pan assemblies. The quartz springs had a coil diameter of 6.4 mm and either 1 mg/mm or 1.25 mg/mm sensitivity (spring rate). The quartz pans were slightly curved with diameters of 7-9 mm and weighed 10-25 mg when empty.

Each vessel was placed in a 41 cm diameter by 30 cm high cylindrical Pyrex jar and completely immersed in Dow Corning silicone bath oil, clear 200 type, with a viscosity of 0.05 Pa · s. For insulation, a 10 mm thick aluminum lid was placed over the jar and 76 mm thick fiberglass sheet was wrapped around the circumference of the Pyrex jar. Two rectangular holes were made so that the view ports were visible. The bath was heated using a 1000 W Vycor (Corning Incorporated trademark) immersion heater and stirred to maintain temperature uniformity using a 37 W Cole-Parmer Stir-Pak mixer with a 51 mm diameter propeller. The temperature was monitored using a Fluke thermometer with a type K thermocouple and 0.1 °C resolution.

A pressure charging and recovery system was designed and built to allow the admission of the agent into the previously evacuated vessel and the recovery of the agent after each measurement. The system was also capable of overpressurizing the vessels with nitrogen but this capability was not employed. The pressure was monitored using a Druck DPI 602 digital pressure indicator and PDCR 910 transducer with an absolute pressure range of 0-6.21 MPa, combined nonlinearity, hysteresis and repeatability of $\pm$ 0.1% using the best straight line method (BSL).

8.2.2.2 Experimental Materials. The elastomers and lubricants used in this study are shown in Tables 1 and 2, respectively. Both crosslinked and uncrosslinked elastomers were studied. The 85% butadiene-15% acrylonitrile crosslinked copolymer was prepared by first dissolving approximately 2 g of polymer in 50 ml of benzene. Next, one part dicumyl peroxide per hundred parts butadiene rubber (1 phr) was added and dissolved. The benzene was allowed to evaporate and the specimen was placed in an oven at 150 °C for a period of 2 hours in order to crosslink the peroxide containing specimen. The 55% butadiene-45% acrylonitrile copolymer was crosslinked in a similar manner using pyridine as the solvent. The silicone, fluorosilicone, and neoprene polymers were supplied crosslinked and uncrosslinked by the vendor. The fluorocarbon polymers were cured at NIST for 1 hour at 150 °C and post-cured at 240 °C for 24 hours.

8.2.2.3 Experimental Methods. Samples of the three greases, six crosslinked and six uncrosslinked polymers weighing 25-50 mg were placed on 15 quartz pans. A glass bead with an

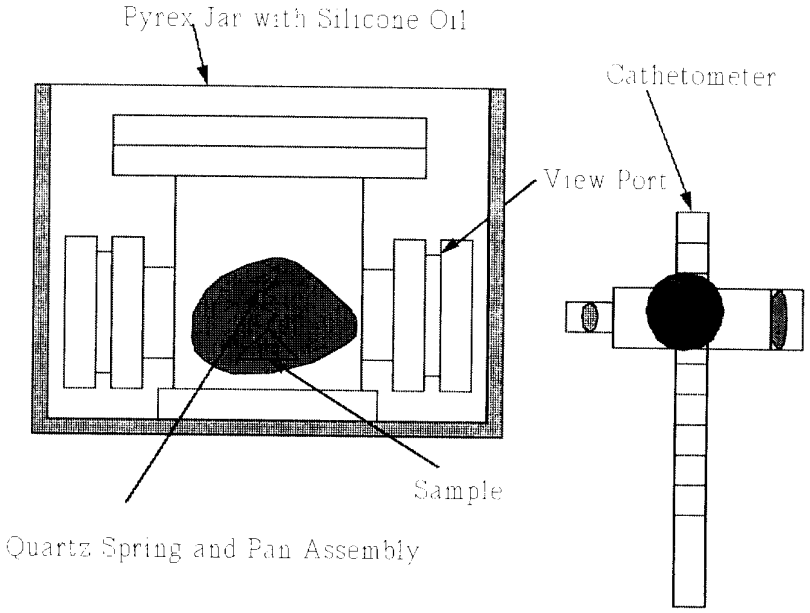

Figure 1. Schematic of the experimental apparatus for isopiestic swelling measurements.

Table 1. Elastomers used in swelling experiments

Elastomer	Vendor	Designation
Silicone	Colonial Rubber	Si
55% Butadiene-45% Acrylonitrile	Goodyear	N206
Fluorosilicone	Colonial Rubber	FSi
Viton E-60 Fluorocarbon	Du Pont	FKM
Neoprene	Colonial Rubber	CR
85% Butadiene-15% Acrylonitrile	Goodyear	N926

Table 2. Lubricants used in swelling experiments

Lubricant	Vendor	Designation
Krytox 240AC Fluorinated Grease	Du Pont	240AC
Braycote 600 Perfluoropolyether Grease, Low Volatility	Castrol	600
Braycote 807 Aircraft Grease MIL-G-27617, Type IV	Castrol	807

approximate mass of 50 mg and volume of 0.02 cm^3 was placed on a sixteenth pan to correct for buoyancy effects. The 16 pans were suspended from quartz springs which were hung on the spring stand and placed in the pressure vessel described above and shown in Figure 1. After aligning the spring stand so that all 16 springs were visible through the view port, the lid of the vessel was bolted in place and the vessel was completely immersed in silicone bath oil. The aluminum lid was placed over the Pyrex jar and the mixer, heater and thermoregulator were adjusted to maintain the maximum test temperature. After evacuation and temperature equilibrium was achieved, the displacements of the calibrated springs were measured using a cathetometer. Next, the pressure was increased to the maximum pressure considered.

Following a swelling equilibration time, which was determined independently and checked, the displacements of the springs were measured again for each sample. The vapor pressure was then decreased to the next lower value, allowed to equilibrate and then measurements were taken. The process was repeated for the remaining pressures considered. The thermoregulator was then reset for the next lower temperature and the system was allowed to equilibrate overnight. After measurements were obtained for all temperatures considered, the vessel was evacuated and the spring displacements were checked for reversibility.

This method of increasing the temperature and pressure to the maximum value considered and then reducing the pressure in increments (instead of increasing the pressure incrementally from a vacuum) was used in order to minimize the disruption of the system which occurs when pumping at

high pressures. The undesired saturation condition and associated liquid condensation, which could ruin the measurements, was also more easily avoided.

In this work, swelling measurements at four vapor pressures were taken for each temperature and were usually done in the morning after equilibration overnight and in the late afternoon after equilibration during the working hours. Measurements were taken at 35, 70, 105, and 150 °C. In addition, FC-116 (hexafluoroethane) was also tested at 5 °C (p^o=2.133 MPa) because this fluid has a low critical temperature (T_c = 19.7 °C) and little swelling was observed at temperatures above T_c. The maximum pressure considered was 5.86 MPa. For test temperatures above the critical temperature of the agent, vapor pressures were chosen to cover the range from the maximum pressure (5.86 MPa) to the saturation pressure of the highest test temperature for which saturation occurs. For temperatures below T_c, vapor pressures were chosen to cover the range from saturation for the test temperature to the saturation pressure of the next lower temperature considered. Saturation pressures for each temperature were determined using thermodynamic properties software (Gallagher *et al.*, 1991; Allied Signal, Inc., 1989) or vendor supplied data (E.I. du Pont de Nemours, Inc., 1968 and 1993; Robin, 1992; Wilson *et al.*, 1992) and are shown in Table 3.

Table 3. Saturation data for agents

Trade name	Formula	Chemical name	p^o @ 35°C	p^o @ 70 °C	p^o @ 105°C	T_c (°C)	p_c (MPa)
HFC-236fa	$CF_3CH_2CF_3$	hexafluoropropane	0.381	1.07	2.11	130.6	3.18
HFC-32/125	CH_2F_2/CHF_2CF_3	azeotrope	2.16	4.74	--[a]	73.2	5.06
HFC-227ea	C_3HF_7	heptafluoropropane	0.615	1.49	--	101.7	2.91
HCFC-22	CHF_2Cl	chlorodifluoromethane	1.35	3.00	--	96.0	4.99
HFC-134a	CH_2FCF_3	tetrafluoroethane	0.887	2.12	--	101.1	4.07
FC-116	C_2F_6	hexafluoroethane	--	--	--	19.7	3.03
HCFC-124	$CHFClCF_3$	chlorotetrafluoroethane	0.516	1.26	2.63	118.9	4.60
HFC-125	CHF_2CF_3	pentafluoroethane	1.78	--	--	66.3	3.62
FC-218	C_3F_8	octafluoropropane	1.15	2.41	--	71.9	2.68
FC-31-10	C_4F_{10}	decafluorobutane	0.364	0.921	1.97	113.2	2.30
FC-318	cyclo-C_4F_8	octafluorocyclobutane	0.428	1.08	2.25	115.2	2.78

[a]not defined

8.2.3 Results and Discussion. In Figures 2-4 typical plots of solvent weight fraction w_1 *vs.* vapor pressure p are shown for different elastomer/agent systems. The solvent uptake of the polymers strongly increases with the vapor pressure. The vertical arrows in the figures show the saturation vapor pressures of the solvent p^o_T at different temperatures. In Figure 4 it is demonstrated that the swelling degree of silicone in decafluorobutane (FC-31-10) significantly decreases with increasing

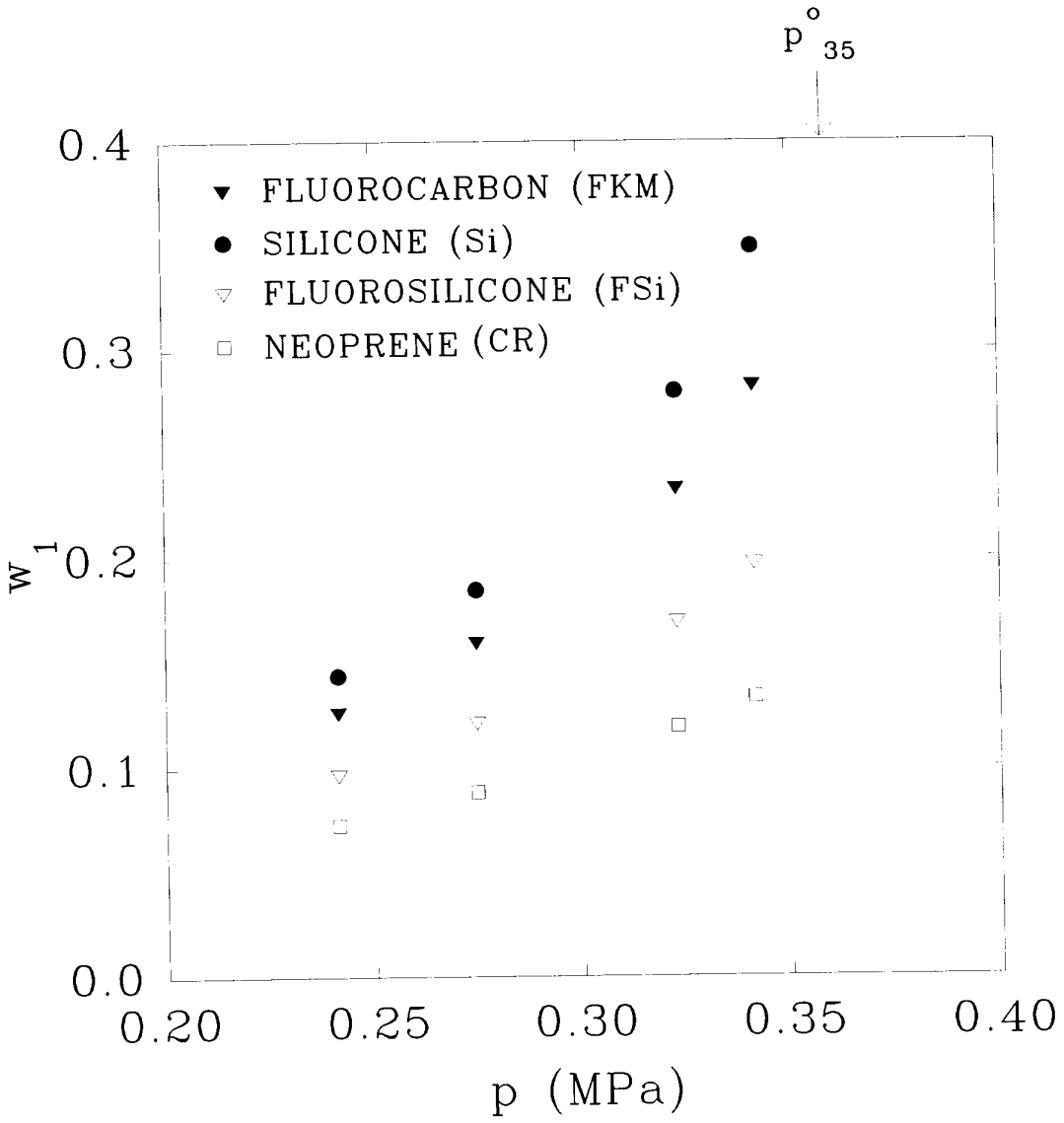

Figure 2. Weight fraction w_1 of FC-31-10 as a function of pressure for various polymers at 35 °C. The arrow shows the saturation vapor pressure p^o = 0.36 MPa of the agent.

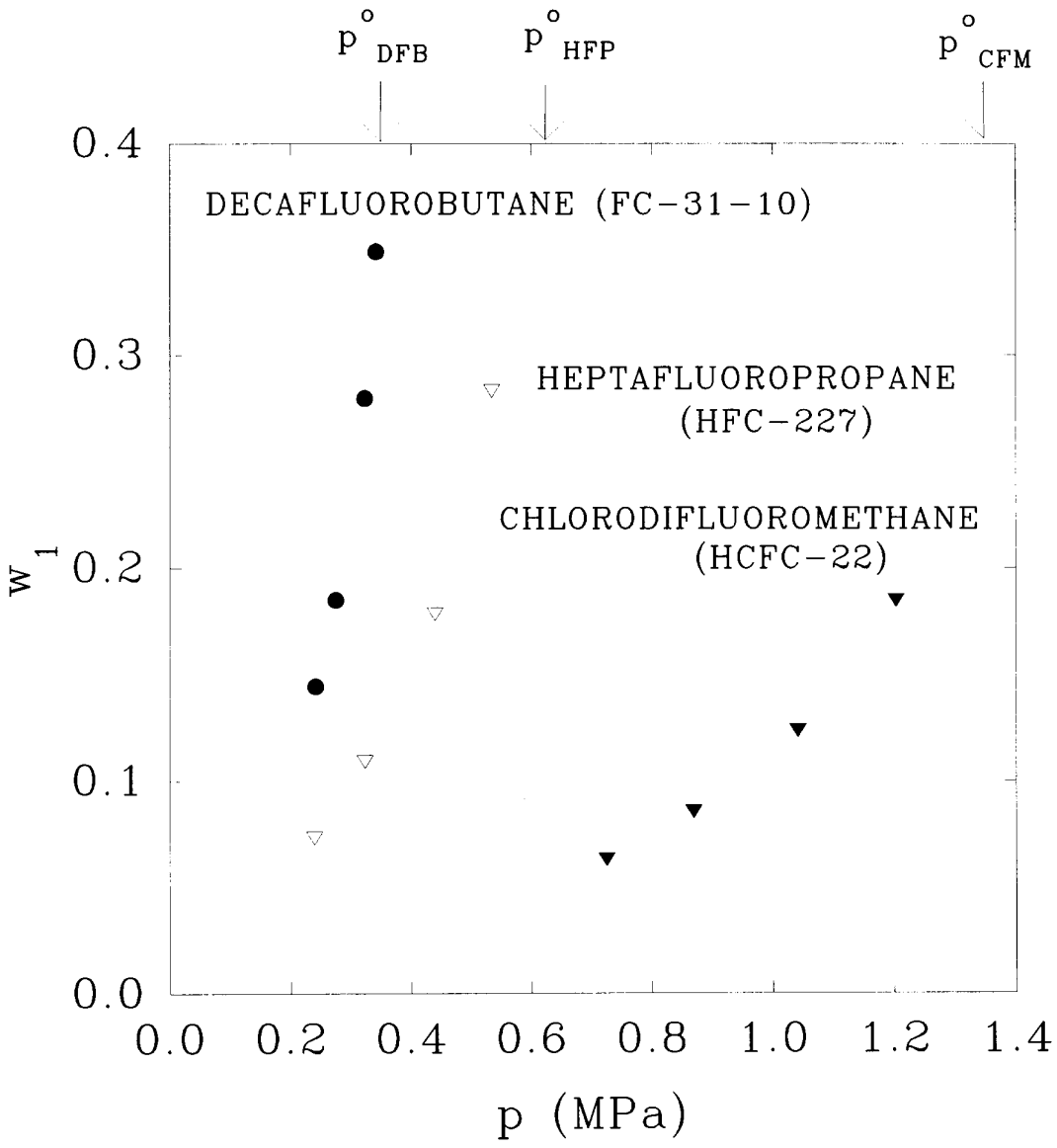

Figure 3. Swelling of uncrosslinked silicone in various agents as a function of pressure at 35 °C. The arrows show the saturation vapor pressures of the respective agents.

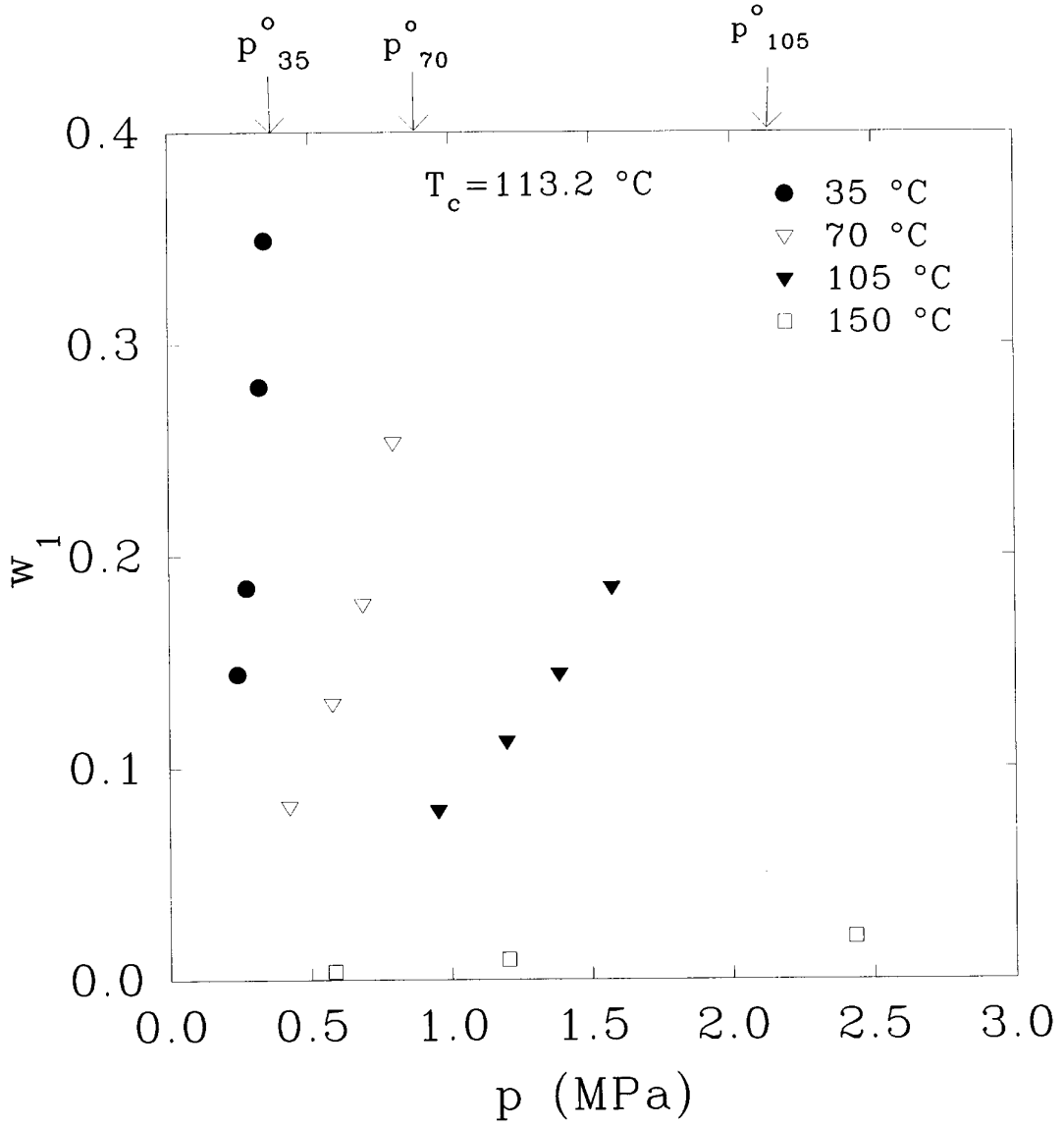

Figure 4. Weight fraction w_1 of FC-31-10 as a function of vapor pressure in uncrosslinked silicone at various temperatures. The arrows show the saturation vapor pressures at the respective temperatures.

temperature. At 150 °C, *i.e.*, above the critical temperature of decafluorobutane (T_c = 113.2 °C), the fluid uptake was approximately one order of magnitude smaller than at 105 °C.

In Figures 5-6, the same experimental data shown in Figures 2-4 are shown according to the Flory-Huggins representation. The continuous curves were calculated using least squares fits of Equation 9 to the data points. The experimental values of ln (p / p^o) *vs.* w_2 were satisfactorily described using a temperature and concentration dependent interaction parameter. The values of the Flory-Huggins interaction parameters ($\chi = \chi_0 + \chi_1$) calculated from solubility data at different temperatures are given in Tables 4 and 5 for all the polymer/solvent systems investigated. The χ values are measures of the solubilities (compatibilities) of the subcritical agents in various polymers. (Small χ values correspond to good solubility or, for present purposes, bad compatibility. Above χ = 0.5, solubility of the polymers gradually decreases with increasing χ.)

In Figure 7 the swelling of crosslinked and uncrosslinked silicone are compared. The difference between the swelling behavior of the two samples is apparent: the crosslinked polymer exhibits considerably lower affinity to the solvent than the uncrosslinked one. The values of the interaction parameters calculated from solubility data at 35 °C for the crosslinked and uncrosslinked polymers are χ = 0.99 and χ = 1.04, respectively. Strictly speaking Equation 9 can only be applied for the uncrosslinked polymer. The appropriate expression for the crosslinked polymer contains an additional term arising from the change in Gibbs free energy due to the elastic deformation of the network on swelling. For lightly crosslinked networks at high polymer concentration ($w_2 > 0.7$), the contribution of the elastic term is negligible in comparison to the mixing term.

Above the critical temperature of the fluid the swelling behavior of the polymers can be analyzed on the basis of Equation 11 (Flory's equation-of-state theory). In Figure 8, the fits of Equation 11 to the swelling data for the silicone/decafluorobutane system at four temperatures between 35 °C and 150 °C are shown. Values of the equation-of-state parameters used in these calculations were obtained from the literature (Shih and Flory, 1972; Wilson *et al.*, 1992). The fit of Equation 9 (Flory-Huggins theory) to the data are also shown in Figure 8 for the three temperatures below the critical temperature T_c = 113.2 °C of FC-31-10 (decafluorobutane). Both theories yield reasonable fits to the experimental data below the critical temperature of the solvent. In addition, Flory's equation-of-state theory yields a reasonable fit to the experimental data above T_c.

In order to rank the agents in terms of their compatibility with the sealing materials, a rating system was defined for the data at 35 °C. This temperature was chosen for several reasons. First, as shown in Figure 4, swelling is greatest at 35 °C and decreases with increasing temperature. Second, it is near the initial storage temperature of 25 °C and third, it is below the critical temperature for every agent considered except FC-116 (hexafluoroethane). FC-116 was rated based on its swelling data at 5 °C because it has a critical temperature of 19.7 °C. A good, bad, or fair rating is given for each agent/crosslinked elastomer and agent/lubricant system in Table 6. Bad compatibility was defined as a condition of excessive swelling and corresponding to $\chi < 0.9$, where χ is the Flory-Huggins polymer-solvent interaction parameter. Good compatibility implies that the elastomer or lubricant is acceptable for use in the fire suppressant system and corresponds to $\chi > 1.2$. For values of χ between 0.9 and 1.2, the agent was considered to have fair compatibility with the elastomer or grease and represents a marginally acceptable system. Under saturation conditions, χ values of 0.9 and 1.2 represent agent weight fractions of 0.38 and 0.22, respectively.

The χ values shown in Tables 4 and 5 were calculated using the curve fitter in the scientific graphing software SigmaPlot for DOS (Jandel, 1992). The curve fitter uses the Marquardt-Levenberg algorithm (Press *et al.*, 1986) to find the parameters which minimize the variance s^2 (ln p / p^o), *i.e.*, the squared differences between the observed and predicted values of the dependent variable. The standard error or experimental standard deviation of the χ parameter, s (χ), and the coefficient of variation, CV = s (χ) / χ x 100, were also calculated for each χ value. Thus, the standard

Table 4. Flory-Huggins interaction parameters χ for the subcritical temperatures studied for each agent/lubricant system considered

Agent (T °C)	Krytox 240AC	Braycote 600	Braycote 807
236fa (35)	1.54	1.60	1.72
236fa (70)	1.53	1.61	1.75
236fa (105)	1.65	1.73	1.88
32/125 (35)	1.98[b]	1.63	1.86[b]
32/125 (70)	2.08	1.66	1.96
227ea (35)	1.14[a]	0.93	0.93[b]
227ea (70)	1.23	0.97	1.02
22 (35)	1.08	1.30	1.20
22 (70)	1.10	1.31	1.23
134a (35)	1.64	1.21	1.76
134a (70)	1.68	1.24	1.65
116 (5)	1.08	1.13	1.05
124 (35)	1.31[b]	1.37[b]	1.31
124 (70)	1.28	1.37	1.30
124 (105)	1.30	1.39	1.33
125 (35)	1.18	1.37	1.35
218 (35)	1.83[b]	1.45	1.76
218 (70)	1.86	1.47	1.79
31-10 (35)	0.93	0.73	0.82
31-10 (70)	0.95	0.75	0.83
31-10 (105)	1.01	0.80	0.88
318 (35)	1.03	1.00	1.00
318 (70)	1.04	1.03	1.01
318 (105)	1.10	1.10	1.10

[a] $12.5 < CV < 20\%$ and $0.64 < \chi < 1.5$ (35 °C)
[b] $CV > 20\%$ (35 °C)

uncertainty of the parameter χ is $u(\chi) = s(\chi)$ and the percentage of relative standard uncertainty is $u(\chi) / \chi \times 100 = CV$. The expanded uncertainty is $U = k\,u(\chi)$, where k = 2, and the percentage of relative expanded uncertainty is $U / \chi \times 100 = k\,CV$.

Unless otherwise indicated in Tables 4, 5, and 6, the coefficient of variation was less than 12.5% for the χ parameters at 35 °C which gives a percentage of relative expanded uncertainty of 25%.

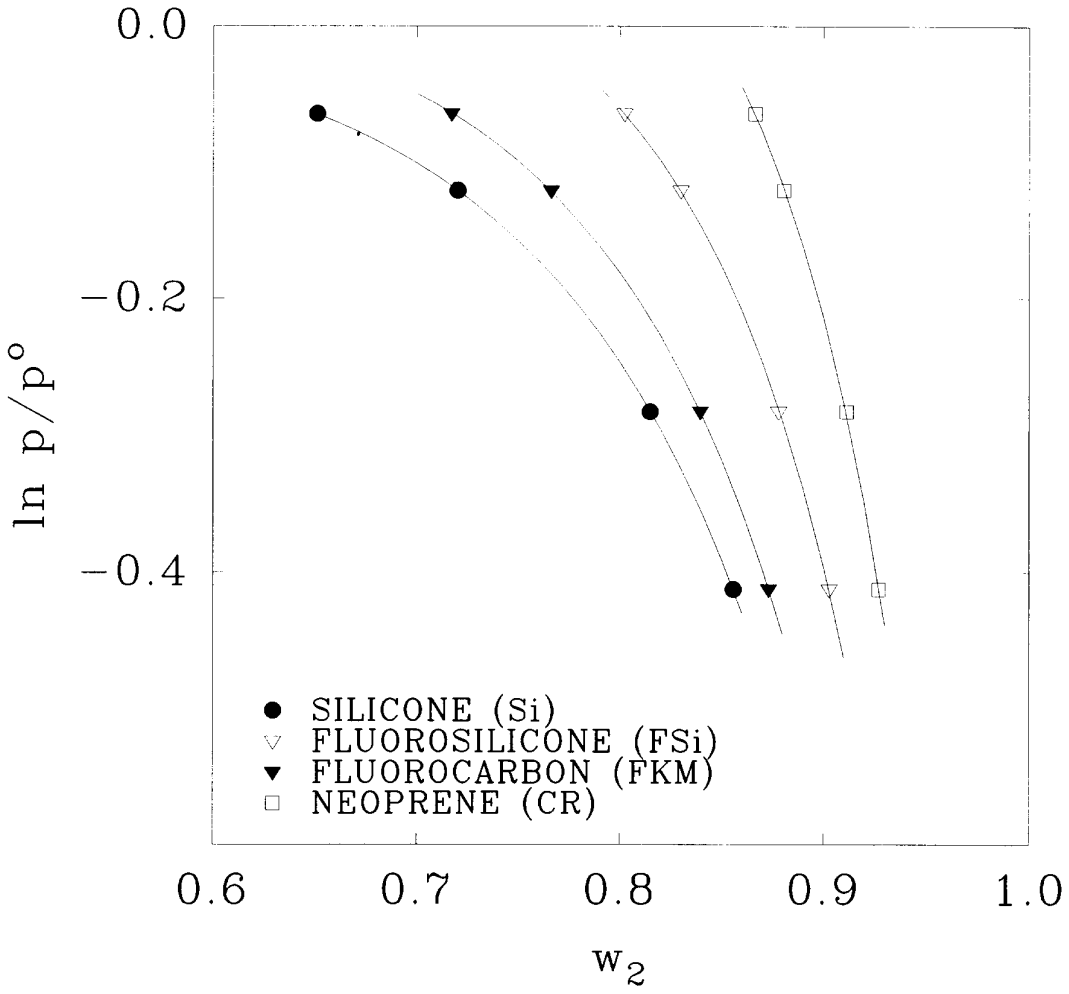

Figure 5. Solvent activity in various polymers in FC-31-10 as a function of polymer weight fraction w_2 at 35 °C. The continuous curves show the least squares fits according to Equation 9.

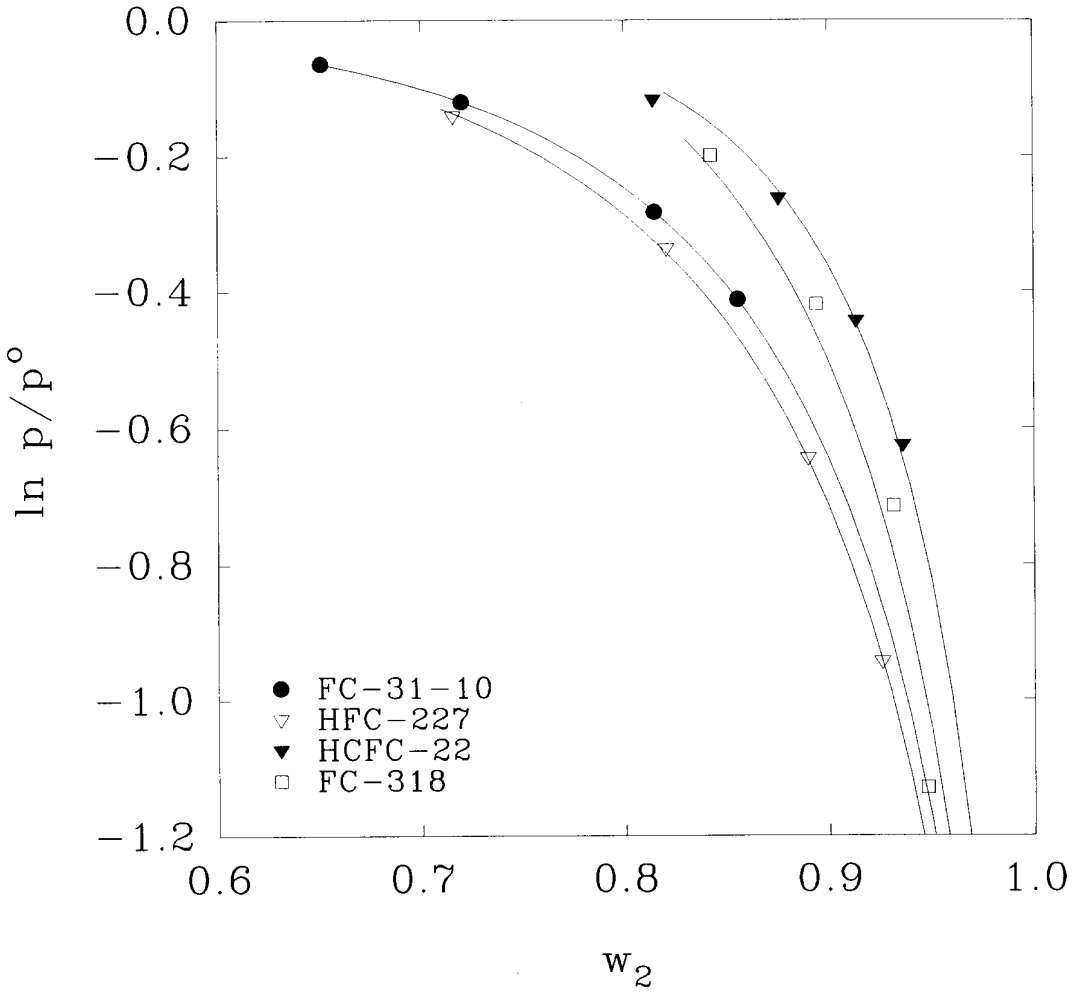

Figure 6. Solvent activity in uncrosslinked silicone as a function of the polymer weight fraction w_2 at 35 °C in various agents. The continuous curves show the fits according to Equation 9.

Table 5. Flory-Huggins interaction parameters χ for subcritical temperatures studied for each agent/elastomer system considered

Agent (T °C)	u[c] Si	x[d] Si	u N206	x N206	u FSi	x FSi	u FKM	x FKM	u CR	x CR	u N926	x N926
236fa (35)	1.09	1.10	1.02	1.05	0.66	0.68	0.76	0.77	0.81	0.84	0.60	0.64
236fa (70)	1.08	1.12	1.03	1.07	0.68	0.71	0.77	0.79	0.83	0.85	0.61	0.65
236fa (105)	1.12	1.15	1.19	1.20	0.76	0.79	0.81	0.83	0.90	0.92	0.84	0.86
32/125 (35)	1.03	1.06	1.48	1.52[b]	1.24[b]	1.28	1.14[b]	1.19	1.12	1.16	1.37	1.41[b]
32/125 (70)	1.08	1.13	1.51	1.56	1.27	1.34	1.18	1.23	1.16	1.15	1.41	1.47
227ea (35)	0.89	0.93[a]	1.34[b]	1.40[b]	0.97	1.04[a]	1.01	1.07[b]	1.25[b]	1.33[a]	0.80	0.84
227ea (70)	0.94	0.96	1.48	1.50	1.10	1.13	1.09	1.13	1.31	1.38	0.85	0.87
22 (35)	0.98	1.00	0.72	0.75	1.02	1.05	0.97	1.02	1.20[b]	1.26	0.76	0.81
22 (70)	0.99	1.00	0.74	0.75	1.05	1.07	0.99	1.06	1.26	1.28	0.78	0.82
134a (35)	1.16	1.20	1.35	1.36	1.00	1.02	1.25	1.30	1.96	2.00[b]	1.42	1.44
134a (70)	1.19	1.22	1.37	1.38	1.02	1.06	1.28	1.31	2.03	2.04	1.44	1.46
116 (5)	1.41[a]	1.47[a]	1.94[b]	1.92[b]	1.35[b]	1.42	1.33[a]	1.40	1.60	1.68[b]	2.11[b]	2.27[b]
124 (35)	0.88[b]	0.91[b]	0.88[b]	0.92[b]	0.93[b]	0.95[b]	0.96[b]	0.97[b]	0.97[b]	0.98[b]	0.91[b]	0.94[b]
124 (70)	0.85	0.88	0.86	0.89	0.90	0.93	0.95	0.96	0.96	0.98	0.89	0.92
124 (105)	0.86	0.91	0.91	0.94	0.93	0.95	0.97	0.97	0.98	1.01	0.92	0.96
125 (35)	1.29	1.30	1.69[b]	1.72	1.33	1.35	1.18	1.21	4.10[b]	1.99	1.23	1.28
218 (35)	1.55	1.62	1.77[b]	1.84	1.56[b]	1.64	1.65	1.65	1.63	1.68	1.56[b]	1.71
218 (70)	1.64	1.69	2.04	1.99	1.67	1.74	1.66	1.67	1.75	1.77	1.69	1.74
31-10 (35)	0.99	1.03	1.18	1.24	1.32	1.39	1.09	1.15	1.55	1.59	1.10	1.13
31-10 (70)	1.01	1.06	1.20	1.25	1.35	1.44	1.13	1.19	1.58	1.66	1.13	1.15
31-10 (105)	1.09	1.09	1.30	1.31	1.40	1.45	1.18	1.25	1.60	1.64	1.19	1.23
318 (35)	1.04[b]	1.27	1.41	1.46	1.27	1.32[a]	1.32	1.34	1.32[b]	1.35	1.10	1.14
318 (70)	1.26	1.29	1.46	1.47	1.27	1.33	1.33	1.36	1.32	1.38	1.10	1.16
318 (105)	1.29	1.37	1.52	1.56	1.33	1.37	1.41	1.44	1.34	1.39	1.19	1.23

[a] $12.5 < CV < 20\%$ and $0.64 < \chi < 1.5$ (35 °C)
[b] $CV > 20\%$ (35 °C)
[c] uncrosslinked polymer
[d] crosslinked polymer

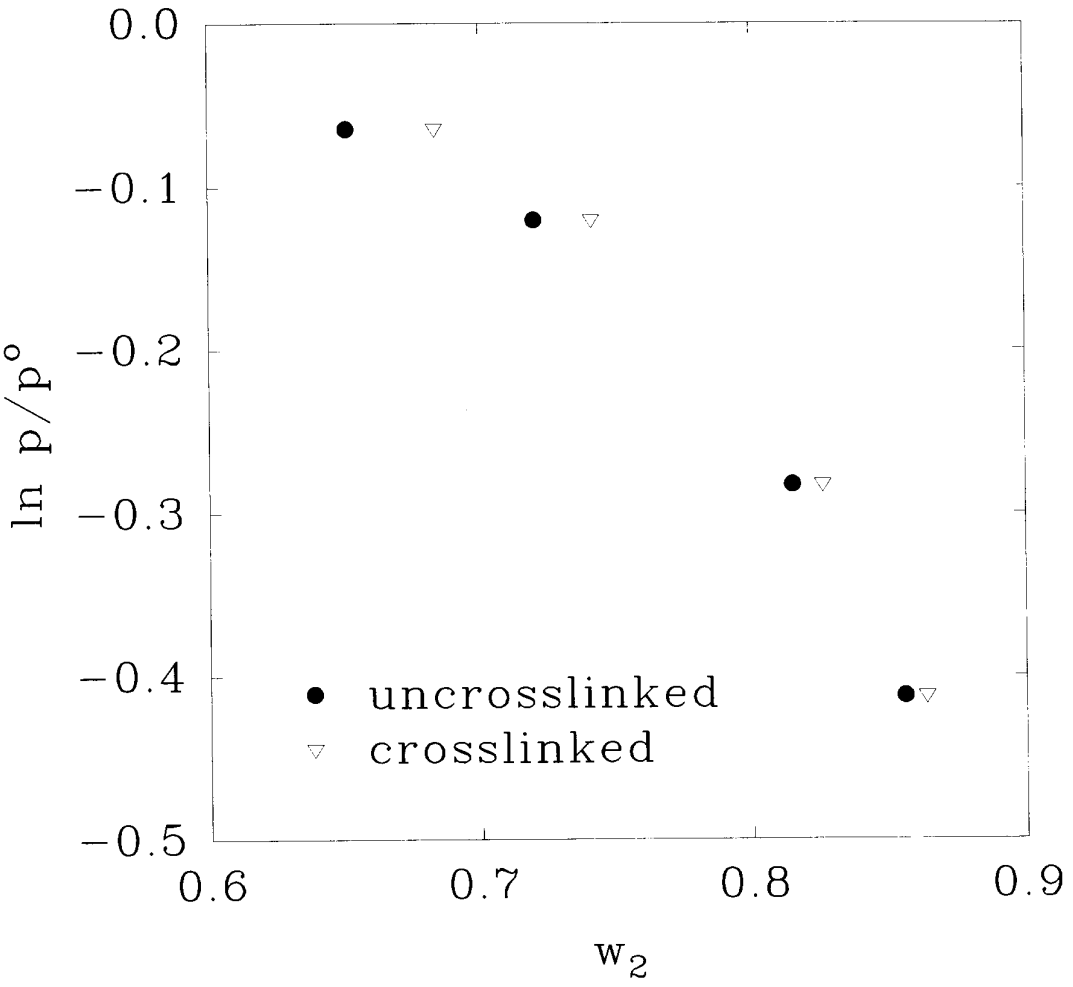

Figure 7. Comparison between the swelling of crosslinked and uncrosslinked silicone in FC-31-10 at 35 °C.

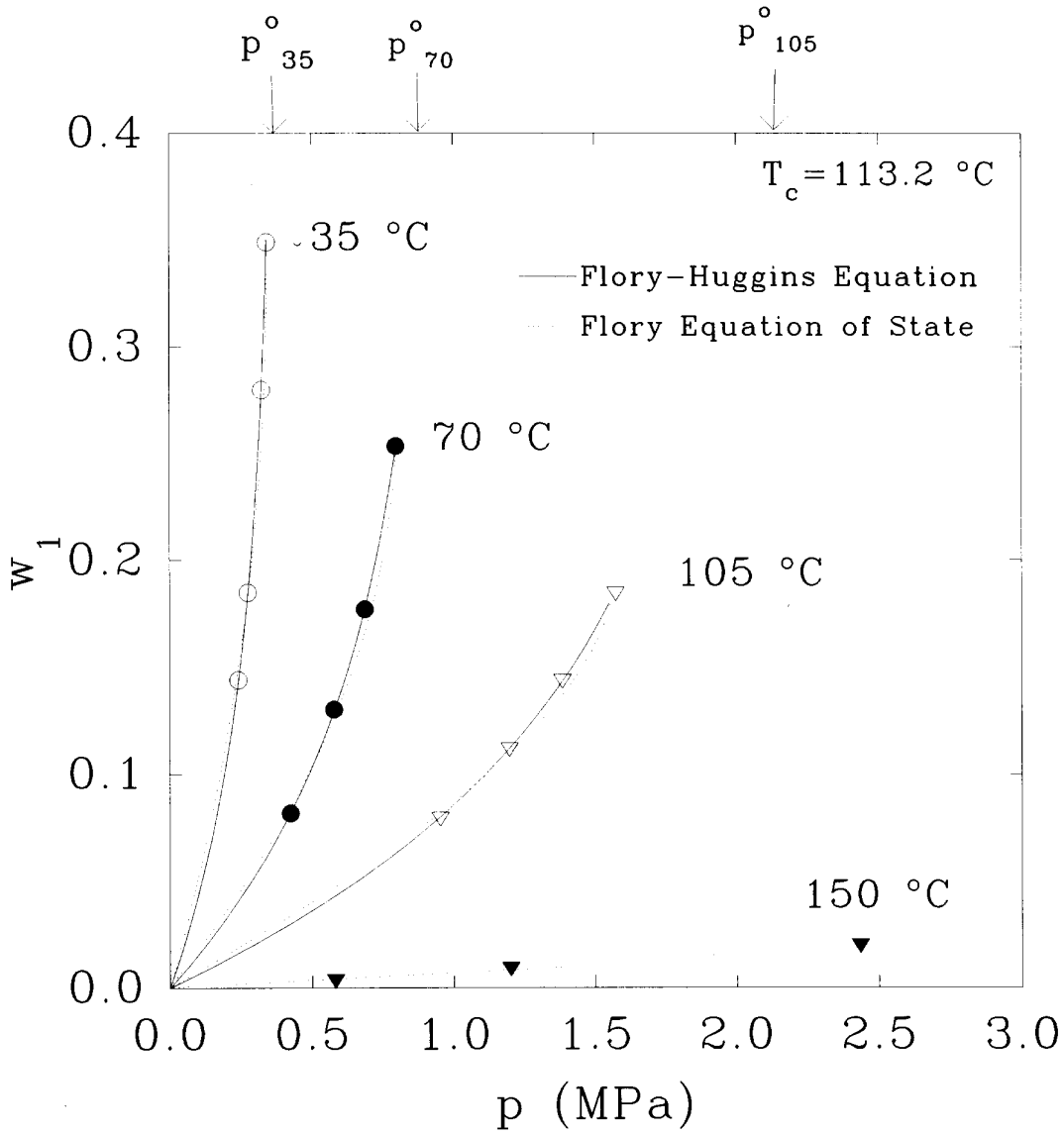

Figure 8. Comparison between measured and calculated values of the weight fraction w_1 of FC-31-10 in silicone.

Hence, for an estimated χ value of 1.2, the measurand (true value of χ) is 1.2 $\pm$ 0.3. This level of confidence suggests that an agent which was assigned a good rating with a χ value slightly greater than 1.2 may actually fall into the fair range ($0.9 < \chi < 1.2$) but a bad rating ($\chi < 0.9$) is statistically unlikely. A similar argument can be made for an agent with a bad rating and an estimated χ value slightly less than 0.9.

The agent/polymer systems for which $0.64 < \chi < 1.5$ and $12.5 < CV < 20\%$ at 35 °C are shown in Tables 4 and 5 with superscripts. If $\chi = 1.5$ and $CV = 20\%$, the value of the measurand is 1.5 $\pm$ 0.6 and the agent may fall into the fair range but a bad rating ($\chi < 0.9$) is statistically unlikely. Similarly, if $\chi = 0.64$ and $CV = 20\%$, the value of the measurand is 0.64 $\pm$ 0.26 and the agent may fall into the fair range but a good rating ($\chi > 1.2$) is statistically unlikely.

Estimated values of χ for which $CV > 20\%$ are also shown with superscripts in Tables 4 and 5. In some instances, the uncertainty represented by large coefficients of variation may be attributed to the small degree of swelling ($w_2 \approx 1.0$) in poor solvents. Using the idealization that the mixing contribution to the chemical potential is zero gives the expression

$$\chi = -\frac{\ln(1 - w_2) + w_2}{w_2^2}, \tag{14}$$

where the slope of χ goes to infinity as $w_2 \rightarrow 1.0$. Hence, small errors in w_2 due to uncertainty in the cathetometer readings ($\pm$ 0.05 mm) produce large differences in the estimate of χ as $w_2 \rightarrow 1.0$ because $-\ln(1 - w_2) \rightarrow \infty$.

8.3 Durability

8.3.1 High Temperature Exposure Methods. As an independent method of characterizing the compatibility of fire suppressant agents, mechanical property measurements of the elastomers and greases were obtained after short term exposures to the agents at extreme conditions of 150 °C and 5.86 MPa. For this purpose, two separate pressure vessels without view ports were designed and built. These pressure vessels were also made of stainless steel and designed for a maximum working pressure of 5.86 MPa. The cylindrical vessel had 10 liters of inner volume (25 cm height by 23 cm diameter) and was large enough to fit an 18 cm diameter compression set fixture, (20) samples for each of the six elastomers, and a 2 ml vial for each of the three greases.

After placing the test samples in the vessel, it was placed in a Fisher Scientific Isotemp forced air lab oven with an inside capacity of 51 x 61 x 51 cm, temperature range of 30 to 200 °C with 1 °C resolution, $\pm$ 3 °C accuracy and $\pm$ 3 °C uniformity. After evacuating the vessel, the charging and recovery system described previously was used to pump a predetermined mass of agent into the chamber at room temperature (24 $\pm$ 1 °C). The value of mass necessary to obtain 5.86 MPa at 150 °C was determined using thermodynamic properties software (Gallagher *et al.*, 1991; Allied Signal, Inc., 1989) or vendor supplied data (E.I. du Pont de Nemours, Inc., 1968 and 1993; Robin, 1992; Wilson *et al.*, 1992).

The oven was turned on, set to 150 °C, and monitored using a Fluke thermometer with a type K thermocouple and 0.1 °C resolution. The pressure was monitored using a Druck DPI 602 digital pressure indicator and PDCR 910 transducer with an absolute pressure range of 0-6.21 MPa, combined nonlinearity, hysteresis and repeatability of $\pm$ 0.1% using the best straight line method (BSL). After attaining thermal equilibrium, the pressure was reduced until the desired pressure of

Table 6. Compatibility of lubricants and crosslinked elastomers based on swelling measurements in various fluorocarbon agents at 35 °C

Agent	240AC	600	807	Si	N206	FSi	FKM	CR	N926
HFC-236fa	good[a]	good	good	fair[b]	fair	bad[c]	bad	bad	bad
HFC-32/125	good[f]	good	good[f]	fair	good[f]	good	good	good	good[f]
HFC-227ea	fair[e]	fair	fair[f]	fair[e]	good[f]	fair[e]	fair[f]	good[e]	bad
HCFC-22	fair	good	fair	fair	bad	fair	fair	good	bad
HFC-134a	good	fair	good	fair	good	fair	good	good[f]	good
FC-116[d]	fair	fair	fair	good[e]	good[f]	good	good	good[f]	good[f]
HCFC-124	good[f]	good[f]	good	bad[f]	fair[f]	fair[f]	fair[f]	fair[f]	fair[f]
HFC-125	fair	good	good	good	good	good	fair	good	good
FC-218	good[f]	good	good	good	good	good	good	good	good
FC-31-10	fair	bad	bad	fair	fair	good	fair	good	fair
FC-318	fair	fair	fair	good	good	good[e]	good	good	fair

[a] $\chi > 1.2$
[b] $0.9 \leq \chi \leq 1.2$
[c] $\chi < 0.9$
[d] measured at 5 °C
[e] $12.5 < CV < 20\%$ and $0.64 < \chi < 1.5$
[f] $CV > 20\%$

5.86 MPa was achieved. The pressurized vessel was then left undisturbed until the exposure time was completed. Short term exposure times of one, 2, 4, and 6 weeks were considered for the initial screening of the agents. After the completion of each exposure, the oven was turned off and the agent was recovered into an evacuated storage cylinder immersed in a water bath.

To maintain the project time schedule, two of the small pressure vessels used for swelling measurements were used as containers for additional high temperature exposures. The procedure described above was followed except a silicone oil bath setup similar to that used for the swelling measurements was employed for heating. However, in order to expedite the sample placement and removal process, the pressure vessels were only partially (approximately half) immersed in the silicone oil. This allowed for the removal of the vessel's top without waiting for the silicone oil to cool and eliminated subsequent pumping of oil to access the samples. The compression set fixtures and lubricant samples were placed near the bottom of the vessel, below the level of the silicone oil. The tensile test samples were placed on top of the compression set fixtures. Some were above and some were below the level of the silicone oil.

A set of tests was conducted in which two thermocouples were placed inside a small pressure vessel filled with air at ambient pressure (high pressure agent could not be used because of leaks due to the presence of the thermocouples). One was placed near the bottom and the other near the top of the vessel. A third thermocouple was immersed in the silicone oil bath which was heated to 150 °C.

These tests show that temperature within the pressure vessel may have varied from 140 to 149 °C when the temperature of the silicone oil was 150 °C. During the actual experiments, this variation was probably less due to the larger heat conduction (relative to air) of the supercritical fluids at 5.86 MPa.

This setup was used for high temperature exposures of FC-116 (hexafluoroethane), FC-218 (octafluoropropane), FC-31-10 (decafluorobutane), and FC-318 (octafluorocyclobutane). As will be shown in the following sections, high temperature exposures to these agents were severe for most of the elastomers and lubricants. Consequently, the results show that exposures throughout the entire temperature range of 140-150 °C are severe.

8.3.2 Elastomers

8.3.2.1 Experimental Materials. The o-rings used in this study were Parker No. 2-214 with a nominal cross section diameter of 3.2 mm (1/8 in.), actual cross section diameter of 3.53 ± 0.10 mm, and a mean outside diameter of 3.2 cm. The Parker compounds considered are listed in Table 7.

Table 7. Elastomers used in durability experiments

Elastomer	Vendor	Designation
Silicone	Parker	S604-70[a]
Nitrile (standard industrial)	Parker	N674-70
Fluorosilicone	Parker	L1120-70
Fluorocarbon	Parker	V1164-75
Neoprene	Parker	C1185-70
Nitrile (low temperature industrial)	Parker	N103-70

[a]The number following the dash in the designation (compound number) represents the Shore hardness of the elastomer.

8.3.2.2 Compression Set Measurements. Compression set tests were conducted per standard test methods (ASTM, 1989 and 1990b). Measurements were taken after the one, 2, 4, and 6 week exposure times. For this purpose, eight compression set fixtures were designed and built. Each fixture consisted of two 18 cm diameter and 12.7 mm thick plates, seven spacers 19 mm in diameter and 2.65 ± 0.01 mm thick, and seven sets of 10 mm bolts, nuts, and washers. The plates were made of stainless steel 304, ground to a maximum roughness of 250 nm, chrome plated and polished. The spacers were also made of stainless steel 304 and their thickness was specified to be 75% of the actual mean value of the o-rings (0.75 x 3.53 mm).

Specimens were prepared by cutting 52 mm sections from sample o-rings. The original thickness of each specimen was measured using a hand micrometer with a 6 mm diameter hemispherical tip.

Measurements were taken at four marked locations equally distributed around the circumference in both the radial and axial direction. The average reading was used for subsequent calculations. Two specimens of each compound were placed into a fixture and closed by tightening the bolts in a criss-cross manner so that the plates were drawn together uniformly. The compression set fixtures were placed in a vessel at the beginning of each high temperature exposure. After the pressure vessel was removed from the oven, the compression set fixture was removed from the vessel and the specimens were placed on a poor conducting surface (wood table) and allowed to cool at room temperature for 30 minutes. After the rest period, the thickness measurements were made as described above at the same marked locations. The same specimens were used for all exposures (one, 2, 4, and 6 weeks) to a given agent.

The compression set C_B was calculated using the average thickness readings before and after the exposure and is expressed as a percentage of the original deflection as follows:

$$C_B = \frac{t_o - t_i}{t_o - t_n} \times 100 \ , \tag{15}$$

where t_o and t_i are the original and final thickness, respectively. $t_n = 2.65$ mm is the thickness of the spacers used in the compression set fixtures. This calculation was made for both specimens of each compound after each exposure. The average of these two values was reported as the compression set C_B.

Table 8 shows the experimental values of compression set for each of the compounds after exposures of one, 2, 4, and 6 weeks at 5.86 MPa and 150 °C in each fluorocarbon agent. In some instances, the specimen was split or broken after a given exposure time. For these cases, the compression set measurements were still taken but the value is superscripted in Table 8.

In Table 9, compatibility ratings of the agents based on compression set measurements of each elastomer are shown. Bad compatibility was defined as a condition when the compression set exceeded 90% after a 2 week exposure. Elastomers have good compatibility if the compression set was less that 90% after 4 weeks. If the compression set was less than 90% after 2 weeks but exceeded 90% after a 4 week exposure, the agent was considered to have fair compatibility with the elastomer and represents a marginally acceptable system. If a specimen was split or broken, the agent was considered to have bad compatibility with the elastomer.

As specified in Option 1 of the standards for compression set (ASTM, 1989 and 1990b), the value of compression set for each elastomer/agent system reported in Table 8 is the average of the compression set calculated from measurements of two samples. The experimental standard deviation $s\ (C_B)$ and the standard uncertainty of the mean $u\ (C_B) = s\ (C_B) / \sqrt{n}$, where $n = 2$ is the number of samples, were also calculated. The coefficient of variation is $CV = u\ (C_B) / C_B$ x 100, the expanded uncertainty is $U = k\ u\ (C_B)$, where k = 2, and the percentage of relative expanded uncertainty is $k\ CV$. The maximum value of CV was 10%. Hence, for an estimated compression set of 90%, the measurand (true value) is 90 ± 18%. This level of confidence suggests that an elastomer with an estimated compression set value of approximately 90% after 4 weeks may fall into the good or fair category. However, in order for an elastomer assigned a good rating to actually have bad compatibility, the estimate for compression set based on a separate set of data after 2 weeks must also exceed 90% which is unlikely because compression set decreases monotonically with decreasing exposure time. Similar arguments can be made for elastomers with estimated compression set values of approximately 90% after 2 weeks.

8.3.2.3 Tensile Testing. Tensile tests were conducted per standard test methods (ASTM, 1990a and 1990b). For each agent, twenty sample o-rings of each compound were tied together with wire

Table 8. Compression set measurements after 1, 2, 4, and 6 week exposures at 5.86 MPa and 150 °C in various fluorocarbon agents

Compound (weeks)	236fa	32/ 125	227ea	22	134a	116	124	125	218	31-10	318
S604-70 (1)	27	34	25	16	35	30	11	33	41	41	31
S604-70 (2)	38	36	34	28	37	41	26	36	48	50	35
S604-70 (4)	52	48	48	66	47	53	35	50	50	61	45
S604-70 (6)	56	69	57	109[a]	59	61	59[a]	58	52	62	51
N674-70 (1)	81	79	77	76	84	59	98	70	77	78	61
N674-70 (2)	92	92	84	96[a]	87	78	103	84	88	89	82
N674-70 (4)	96	93	93	110[a]	98	90	104	91	92	98	94
N674-70 (6)	98	99[a]	97	113[a]	102	96	104	96	95	98	97
L1120-70 (1)	53	66	51	48	60	64	30	65	68	82	60
L1120-70 (2)	65	78	56	62	54	73	51	65	74	87	65
L1120-70 (4)	88	87	72	86	72	83	69	80	76	91	77
L1120-70 (6)	94	104[a]	83	99	78	88	89	90[a]	79	91	87
V1164-75 (1)	31	41	21	46	36	19	14	35	25	25	62
V1164-75 (2)	47[a]	63	33[a]	100[a]	40[a]	31	30	46[a]	39	39	80
V1164-75 (4)	67[a]	82[a]	60[a]	100[a]	55[a]	55	59[a]	72[a]	56	64	92
V1164-75 (6)	94[a]	99[a]	77[a]	100[a]	94[a]	70[a]	91[a]	90[a]	58[a]	66[a]	95
C1185-70 (1)	69	67	66	68	72	54	96	68	67	71	49
C1185-70 (2)	76	76	75	77	79	68	100	70	79	78	70
C1185-70 (4)	84	78	81	95	86	79	105	80	83	89	79
C1185-70 (6)	86	81	84	100	94	84	107	98	82	90	84
N103-70 (1)	79	81	79	79	82	70	88	73	78	82	62
N103-70 (2)	87	91	87	89	85	82	91	83	87	91	80
N103-70 (4)	93	95	91	110	96	92	94	92	90	97	89
N103-70 (6)	95	98	94	113	99	95	98	83	95	97	93

[a]specimen was split or broken

Table 9. Compatibility of elastomers based on compression set measurements after exposures at 5.86 MPa and 150 °C in various fluorocarbon agents

Agent	S604-70	N674-70	L1120-70	V1164-75	C1185-70	N103-70
HFC-236fa	good[a]	bad[c]	good	good	bad	bad
HFC-32/125	good	bad	fair[c]	bad	fair	bad
HFC-227ea	good	bad	good	good	fair	bad
HCFC-22	good	fair	good	good	fair	fair
HFC-134a	good	bad	good	good	fair	bad
FC-116	good	fair	good	fair	good	bad
HCFC-124	good	bad	good	good	bad	bad
HFC-125	good	bad	good	bad	good	bad
FC-218	good	fair	good	fair	good	bad
FC-31-10	good	bad	good	fair	fair	bad
FC-318	good	fair	good	good	good	fair

[a]compression set is less than 90% after four weeks
[b]compression set is less than 90% after two weeks but exceeds 90% after four weeks
[c]compression set exceeds 90% after two weeks

and stored in a pressure vessel. Ultimate elongation, tensile stress, and modulus measurements were taken after one, 2, 4, and 6 week exposure times. A type TT-B Instron tensile testing instrument was used for this purpose. Grips for testing o-rings were designed and built from low carbon steel. The grips consisted of ball-bearing spools 8.9 mm in diameter and were capable of being brought within 19 mm center-to-center distance at closest approach. Stresses were minimized by lubricating the contact surfaces of the spools with Super-Lube o-ring lubricant.

After the exposure was completed, the pressure vessel was removed as described in the previous section and five samples of each compound were removed, placed in sealed plastic bags and labeled with the agent, compound, exposure time and date. All tensile tests were conducted within a 2 week period near the end of the short term exposures in August 1993. Each specimen's thickness W was measured at four points equally distributed around the circumference in the radial and axial direction using a dial indicator with a contact force of 0.2 N. The average reading was used for calculation. The internal diameter of each specimen was measured using a stepped cone with diametric intervals of 0.50 mm.

The grips were brought together and the o-ring specimen was installed with minimal stretching. The crosshead and recorder were set to a speed of 500 $\pm$ 50 mm/min. A load cell with full scale load ranges of 2, 5, 10, 20, and 50 kg was used. Chart paper with a grid of 2.54 x 2.54 mm was used to plot load *vs.* jaw travel. The charts were labeled with the initial jaw position starting point, load range, agent, compound, sample number, temperature, date, average thickness and inside

diameter. The force F was recorded at rupture and at an elongation of 100% (if the ultimate elongation exceeded 100%).

The tensile strength *T.S.* is the tensile stress at rupture and is calculated as

$$T.S. = \frac{F}{A} , \tag{16}$$

where F is the breaking force and A is twice the cross-sectional area calculated from the thickness W as

$$A = \frac{\pi W^2}{2} . \tag{17}$$

The ultimate elongation *U.E.* is expressed as a percentage of the original inside circumference as follows:

$$U.E. = [\frac{2D + G - C}{C}] \times 100 , \tag{18}$$

where D is the distance between centers of the spool grips at the time of rupture, G is the circumference of one spool (π x spool diameter), and C is the inside circumference (π x inside diameter) of the specimen. Assuming neo-Hookean behavior (Mooney, 1940; Treloar, 1948; Atkin and Fox, 1980), the modulus C_1 is expressed as

$$C_1 = \frac{F}{2A(\lambda^2 - 1/\lambda)} , \tag{19}$$

where F is the tensile force and λ is the stretch ratio in the direction of extension. The center-to-center distance of the spool grips D for a prescribed stretch ratio λ is calculated as

$$D = \frac{1}{2}[\lambda C - G] . \tag{20}$$

The median of three specimens was taken as the characteristic value. Table 10 shows the percent decrease in ultimate elongation for each of the compounds after one, 2, 4, and 6 week exposures at 5.86 MPa and 150 °C in each fluorocarbon agent. In some instances, the o-ring could not be installed without breaking the specimen because of embrittlement due to the high temperature exposure. For these cases, the specimen was considered to have a 100% decrease in ultimate elongation.

In Table 11, ratings for the compatibility of elastomers are shown based on tensile testing after exposures at 5.86 MPa and 150 °C in various fluorocarbon agents. Bad compatibility was defined as a condition when the decrease in ultimate elongation exceeded 65% after a 2 week exposure. Elastomers have good compatibility if the decrease was less that 65% after 4 weeks. If the decrease in ultimate elongate was less that 65% after 2 weeks but exceeded 65% after a 4 week exposure, the agent was considered to have fair compatibility with the elastomer and represents a marginally acceptable system.

Table 10. Percent decrease in ultimate elongation measurements after 1, 2, 4, and 6 week exposures at 5.86 MPa and 150 °C in various fluorocarbon agents

Compound (weeks)	236fa	32 /125	227ea	22	134a	116	124	125	218	31-10	318
S604-70 (1)	-7.1	-8.4	7.52	5.75	1.77	23	12.8	8.41	-1.3	7.08	3.1
S604-70 (2)	-1.3	8.85	10.6	8.85	22.1	8.85	11.5	7.08	6.19	3.1	12.8
S604-70 (4)	18.1	13.7	-1.8	8.85	-13	10.6	-9.7	5.31	9.29	12.8	3.1
S604-70 (6)	-3.1	14.6	-6.2	100	-2.7	18.6	0	10.6	4.42	15	13.3
N674-70 (1)	50.3	57.1	32.9	40.3	43.4	36.6	92	48.9	37.7	46.9	23.4
N674-70 (2)	83.9	87.3	80.7	52.9	90.7	64.9	98.2	74.6	59.1	76	52.6
N674-70 (4)	100	98	100	100	98	84.5	100	95.1	73.7	87.9	73.2
N674-70 (6)	100	98.7	99.8	100	100	93	100	98.7	81.6	95.8	83.5
L1120-70 (1)	-0.6	29.3	17.8	48.9	42.5	17.8	-13	8.62	47.9	25.3	2.87
L1120-70 (2)	5.17	37.4	6.9	29.9	25.3	49.7	-4.6	22.4	31	45.2	29.3
L1120-70 (4)	42.5	80.1	41.4	41.4	60.1	64.2	39.7	56.3	43.2	53.4	52.6
L1120-70 (6)	78.8	100	41.4	62.3	71.3	46.8	46	75.1	43.2	61.3	60.1
V1164-75 (1)	38.1	54.8	53.9	44.2	50	42.2	34.5	59.8	50.9	47.9	58.6
V1164-75 (2)	55.6	68.3	41.2	55.1	43.1	60.6	28.6	69.6	52.8	51.7	41.1
V1164-75 (4)	64.5	76.1	62.5	52.8	61.7	73.2	48.9	70.3	72.2	68.3	47
V1164-75 (6)	76.8	92.5	68.3	65.7	72.9	77.4	46	87.7	76.2	80	66
C1185-70 (1)	36.7	37.9	36.7	26.2	27.7	31.3	78.4	23.8	25	27.7	12.9
C1185-70 (2)	65.8	62.6	63.9	38.7	63.9	27.3	88.6	41	41.4	46.9	36.3
C1185-70 (4)	85.6	78.9	85.2	100	95.5	55.1	97.4	63.9	48.8	69.6	48.8
C1185-70 (6)	97.4	86.6	95.9	100	100	69.5	98.5	88	58.6	77.7	57.4
N103-70 (1)	45.2	48	29.4	13.1	36.1	41.3	95.2	60.8	50.8	39.3	9.13
N103-70 (2)	83.6	88.5	79.9	34.5	94.4	73.7	100	79	72.9	78.5	45.2
N103-70 (4)	100	99.1	99.6	100	100	90	100	94.4	83.5	90.4	72.5
N103-70 (6)	100	100	100	100	100	95	100	100	89	96.4	82.7

Since the standards for tensile testing (ASTM, 1990a and 1990b) specify the characteristic value as the median of three specimens, an expression of uncertainty is not easily determined without additional analysis and/or testing. However, arguments similar to those in Section 8.3.2.2 on compression set can be made. That is, an elastomer with an estimated percent decrease in ultimate elongation of approximately 65% after 4 weeks may fall into the good or fair category but bad

Table 11. Compatibility of elastomers based on tensile testing after exposures at 5.86 MPa and 150 °C in various fluorocarbon agents

Agent	S604-70	N674-70	L1120-70	V1164-75	C1185-70	N103-70
HFC-236fa	good[a]	bad[c]	good	bad	good	fair[b]
HFC-32/125	good	bad	bad	bad	good	bad
HFC-227ea	good	fair	good	bad	good	fair
HCFC-22	bad	bad	good	bad	fair	fair
HFC-134a	good	fair	good	bad	good	fair
FC-116	good	fair	good	bad	good	fair
HCFC-124	bad	bad	good	bad	bad	bad
HFC-125	good	fair	bad	bad	good	fair
FC-218	good	fair	good	bad	good	fair
FC-31-10	good	fair	fair	bad	good	bad
FC-318	good	fair	good	good	good	good

[a]decrease in ultimate elongation is less than 65% after 4 weeks
[b]decrease in ultimate elongation is less than 65% after 2 weeks but exceeds 65 % after 4 weeks
[c]decrease in ultimate elongation exceeds 65% after 2 weeks

compatibility is unlikely. Similar arguments can be made for elastomers with an estimated percent decrease in ultimate elongation of approximately 65% after 2 weeks.

8.3.3 Lubricants. The same types of lubricants used in the swelling experiments (listed in Table 2), *i.e.*, Krytox 240AC, Braycote 600 and 807, were subjected to high temperature exposures and then tested for changes in viscosity.

8.3.3.1 Viscosity Measurements. The original rheological properties of each grease were characterized using the Rheometrics Mechanical Spectrometer Model 800. Approximately 10 mg of grease was evenly placed in a cone and plate fixture with a diameter of 25 mm, cone angle of 0.02 radians, and gap of 0.023 mm. The instrument was used to perform steady shear testing of the sample. During the test, the instrument subjects the sample to a rotational shear at a given shear rate $\dot{\gamma}$ and measures the resulting torque. The instrument analyzes the sample's rotational response and calculates the shear stress τ and steady shear viscosity η.

An open 2 ml vial was filled with approximately 100 mg of grease and placed in the pressure vessel. After each exposure approximately 25 mg of grease was removed and stored in a closed 2 ml vial and labeled with the agent, lubricant name, exposure time, and date. All rheology tests were conducted near the end of the short term exposures. Each grease was subjected to rate sweep measurements. The rate sweep test was used to determine the response of the sample to a range of steady shear rates at room temperature (24 $\pm$ 1 °C). The test was performed with strain rates of $\dot{\gamma}$ = 0.010, 0.016, 0.025, 0.040, 0.063, and 0.100 s^{-1} which correspond to six points in a logarithmic

decade. Figure 9 shows typical results for Krytox 240AC after high temperature exposures to HFC-125 (pentafluoroethane). Note the absence of systematic time dependence of viscosity at 150 °C. The viscosity of the grease increases after 1 week exposure to HFC-125, but then decreases after the remaining exposures. This suggests that the differences are due to experimental uncertainty and no significant chemical degradation occurs. However, in some instances, viscosity measurements were not possible because mobile substances were extracted and the greases became powder-like.

Table 12 lists the number of weeks after which the grease's viscosity was still measurable, *i.e.*, had not become powder-like. Table 13 shows the ratings for the compatibility of lubricants based on the viscosity measurements after exposures at 5.86 MPa and 150 °C in various fluorocarbon agents. Bad compatibility was defined as a condition when the grease became powder-like after a 4 week exposure. Lubricants have good compatibility if the grease did not become powder-like after 6 weeks. If the grease became powder-like after 6 weeks, the lubricant was considered to have fair compatibility with the agent.

Due to the nature of the criteria regarding the powder-like nature of the lubricants, an expression of uncertainty is not readily determined without additional testing. However, arguments similar to those in Section 8.3.2.2 on compression set can be made. That is, a lubricant whose viscosity was still measurable after 6 weeks may fall into the fair category but bad compatibility is unlikely. Similar arguments can be made for lubricants which were powder-like after 4 weeks.

8.4 Summary and Conclusion

In order to investigate the potential for deterioration of the o-ring and its lubricant in the fire suppressant storage system, short term exposure experiments have been conducted and data have been generated on the changes in the properties of various elastomers and greases after exposure to the eleven fluid agents. Isopiestic measurements and durability testing proved to be sensitive methods for characterizing the compatibility of elastomers and lubricants with fluorocarbon agents. However, exposures between 140 and 150 °C were found to be severe for most of the elastomers and lubricants. Additional testing at lower temperatures and for longer times is required to better simulate the in-service conditions.

In Table 14, the compatibility of elastomers and lubricants are shown based on the durability ratings in Tables 9, 11, and 13 (G = good, F = fair, B = bad). If the ratings for compression set and tensile testing were different, the worse compatibility is listed. In parentheses, the ratings based on the swelling compatibility only (Table 6) are listed if different than the durability ratings. The swelling ratings for crosslinked 55% butadiene-45% acrylonitrile (N206) and 85% butadiene-15% acrylonitrile (N926) are listed with the standard industrial nitrile (N674-70) and low temperature industrial (N103-70) compounds, respectively. These ratings are summarized below for the 11 agents. If the ratings for durability and swelling compatibility were different, the worse compatibility is reported.

HFC-236

Lubricants Krytox 240AC, Braycote 600 and 807 have good compatibility and silicone is a fairly compatible elastomer. The nitrile, fluorosilicone, fluorocarbon, and neoprene elastomers are incompatible.

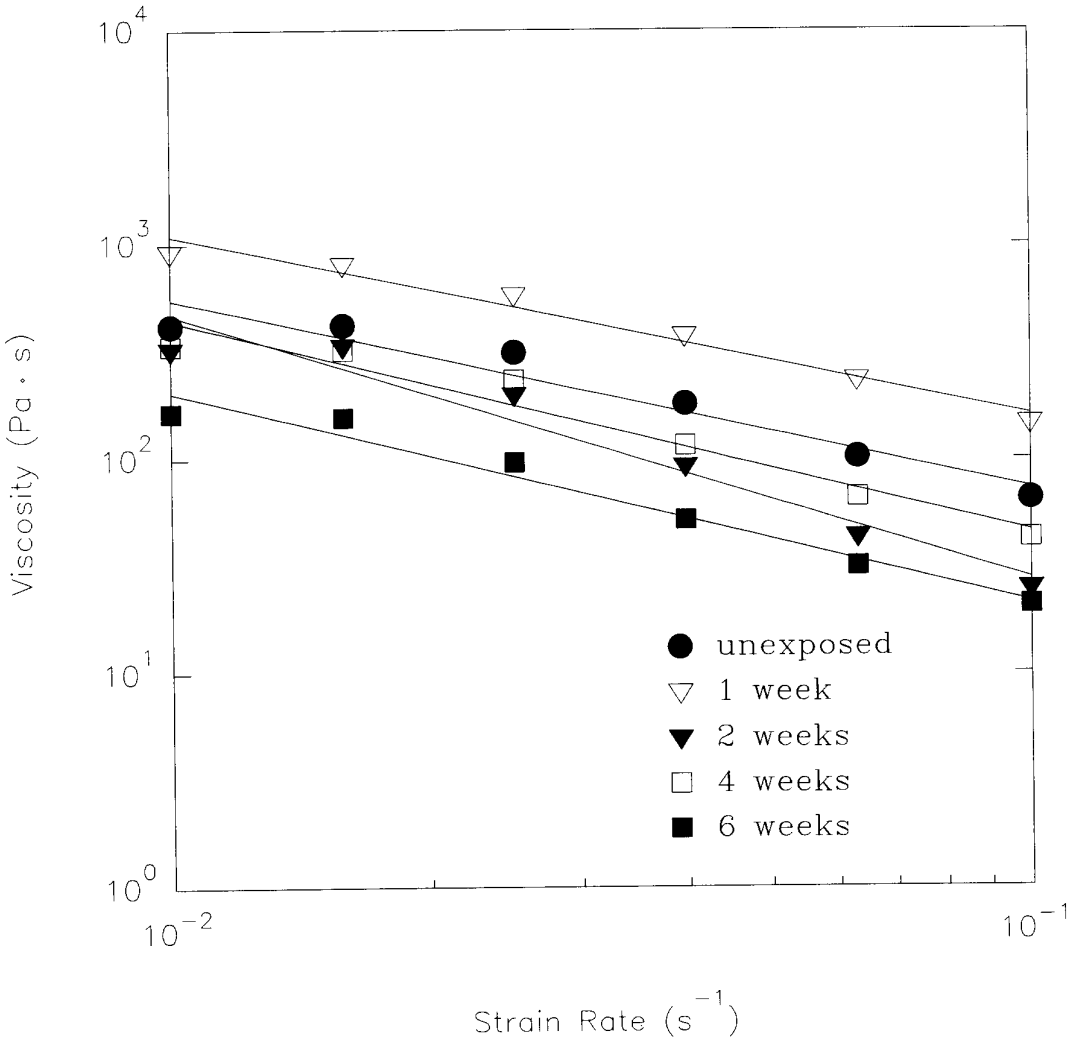

Figure 9. Viscosity measurements of the lubricant Krytox 240AC after various exposure times in HFC-125 (pentafluoroethane) at 150 °C.

Table 12. Number of weeks of exposure at 5.86 MPa and 150 °C in various fluorocarbon agents after which viscosity measurements were still possible, *i.e.*, the grease was not powder-like

Grease	236fa	32 /125	227ea	22	134a	116	124	125	218	31-10	318
Krytox 240AC	6 wks	6 wks	2 wks	2 wks	0 wks	4 wks	6 wks	6 wks	0 wks	0 wks	0 wks
Braycote 600	6 wks	6 wks	6 wks	2 wks	1 wk	6 wks	6 wks	6 wks	2 wks	0 wks	0 wks
Braycote 807	6 wks	6 wks	6 wks	4 wks	0 wks	6 wks	6 wks	6 wks	1 wk	0 wks	0 wks

HFC-32/125

Lubricants Krytox 240AC, Braycote 600 and 807 have good compatibility and silicone and neoprene are fairly compatible elastomers. The nitrile, fluorosilicone, and fluorocarbon elastomers are incompatible.

HFC-227

Braycote 600 and 807 are fairly compatible lubricants and silicone, fluorosilicone, and neoprene are fairly compatible elastomers. Krytox 240AC lubricant and nitrile, fluorosilicone, and fluorocarbon elastomers are incompatible.

HCFC-22

Braycote 807 is a fairly compatible lubricant and fluorosilicone is a fairly compatible elastomer. Krytox 240AC and Braycote 600 lubricants and silicone, nitrile, neoprene, and fluorocarbon elastomers are incompatible.

HFC-134a

Silicone, fluorosilicone, and neoprene are fairly compatible elastomers. Krytox 240AC, Braycote 600 and 807 lubricants and nitrile and fluorocarbon elastomers are incompatible.

FC-116

Krytox 240AC, Braycote 600 and 807 are fairly compatible lubricants. Elastomers silicone, fluorosilicone, and neoprene have good compatibility and nitrile (N674-70) is fairly compatible. Fluorocarbon and nitrile (N103-70) elastomers are incompatible.

HCFC-124

Lubricants Krytox 240AC, Braycote 600 and 807 have good compatibility and fluorosilicone is a fairly compatible elastomer. Silicone, nitrile, and fluorocarbon elastomers are incompatible.

HFC-125

Lubricants Braycote 600 and 807 have good compatibility and Krytox 240AC is a fairly good lubricant. Elastomers silicone and neoprene have good compatibility. Fluorosilicone, nitrile, and fluorocarbon elastomers are incompatible.

Table 13. Compatibility of lubricants based on viscosity measurements after exposures at 5.86 MPa and 150°C in various fluorocarbon agents

Agent	Krytox 240AC	Braycote 600	Braycote 807
HFC-236fa	good[a]	good	good
HFC-32/125	good	good	good
HFC-227ea	bad[c]	good	good
HCFC-22	bad	bad	fair[b]
HFC-134a	bad	bad	bad
FC-116	fair	good	good
HCFC-124	good	good	good
HFC-125	good	good	good
FC-218	bad	bad	bad
FC-31-10	bad	bad	bad
FC-318	bad	bad	bad

[a]grease was not powder-like after 6 weeks
[b]grease was not powder-like after 4 weeks but was powder-like after 4 weeks
[c]grease became powder-like after 4 weeks

FC-218

Elastomers silicone, fluorosilicone, and neoprene have good compatibility and nitrile (N674-70) is fairly compatible. Krytox 240AC, Braycote 600 and 807 lubricants and fluorocarbon and nitrile (N103-70) elastomers are incompatible.

FC-31-10

Silicone, fluorosilicone, and neoprene are fairly compatible elastomers. Krytox 240AC, Braycote 600 and 807 lubricants and nitrile and fluorocarbon elastomers are incompatible.

FC-318

Elastomers silicone, fluorosilicone, fluorocarbon, and neoprene have good compatibility and the nitrile elastomers are fairly compatible. Krytox 240AC, Braycote 600 and 807 lubricants are incompatible.

Table 14. Compatibility of elastomers and lubricants based on the durability ratings in Tables 10, 12, and 14 (G = good, F = fair, B = bad)

Agent	240AC	600	807	S604-70	N674-70 (N206)	L1120-70	V1164-75	C1185-70	N103-70 (N926)
HFC-236fa	G[a]	G	G	G (F)[b]	B (F)	G (B)	B	B	B
HFC-32/125	G	G	G	G (F)	B (G)	B (G)	B (G)	F (G)	B (G)
HFC-227ea	B (F)	G (F)	G (F)	G (F)	B (G)	G (F)	B (F)	F (G)	B
HCFC-22	B (F)	B (G)	F	B (F)	B	G (F)	B (F)	B (G)	F (B)
HFC-134a	B (G)	B (F)	B (G)	G (F)	B (G)	G (F)	B (G)	F (G)	B (G)
FC-116	F	G (F)	G (F)	G	F (G)	G	B (G)	G	B (G)
HCFC-124	G	G	G	B	B (F)	G (F)	B (F)	B (F)	B (F)
HFC-125	G (F)	G	G	G	B (G)	B (G)	B (F)	G	B (G)
FC-218	B (G)	B (G)	B (G)	G	F (G)	G	B (G)	G	B (G)
FC-31-10	B (F)	B	B	G (F)	B (F)	F (G)	B (F)	F (G)	B (F)
FC-318	B (F)	B (F)	B (F)	G	F (G)	G	G	G	F

[a]If the ratings for compression set and tensile testing were different, the worse compatibility is listed
[b]If different, the rating for swelling compatibility (Table 7) is listed in parentheses

8.5 References

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